Available online at www.sciencedirect.com

SciVerse ScienceDirect

Procedia Chemistry 6 (2012) 110 – 116

Procedia Chemistry

2nd International Conference on Bio-Sensing Technology

# Integration of MOSFET/MIM structures using a CMOS-based technology for pH detection applications with high-sensitivity

Joel Molina[a]*, Alfonso Torres[a], Guillermo Espinosa[a], Maria Teresa Sanz[a], Erick Guerrero[a], Berni Perez[a], Jose Fernandez[b], Mazhar Hoque[b] and Patrice Parris[b].

[a]*INAOE, Luis Enrique Erro #1, Tonantzintla, Puebla 72000, Mexico*
[b]*Freescale Semiconductor, Periferico Sur #8110, Col. El Mante,Tlaquepaque, Jalisco 45609, Mexico*

**Abstract**

In this work, we show that by using Metal-Insulator-Metal (MIM) structures integrated in series to the gate of submicron Metal-Oxide-Semiconductor Field-Effect Transistor (MOSFET) devices, highly-sensitive and ultra-low power consumption pH sensors can be obtained. One MIM capacitor enables external polarization of the MOSFET device while a second MIM capacitor is connected to a sensing plate whose surface is whether a thick polyimide layer or the last metallization level. The electrochemical response of these surfaces to pH buffer solutions resembles that of Ion-Sensitive Field-Effect Transistor (ISFET) devices whose pH sensitivity is dependent on the type of surface material being exposed.



*Keywords:* ISFET, MOSFET, MIM capacitor, reference electrode, pH detection, chemical sensor, CMOS processing.

## 1. Introduction

Since their invention in 1970 [1], ISFET-based chemical sensors have relied on the transduction of electrochemical signals to current/voltage levels which are proportional to the ionic activity of the ions of interest. This is done with the MOSFET structure, in which its poly-silicon or metal-gate material is completely removed so that the surface of its gate oxide is directly exposed to the ionic activity of the solutions to measure. Once the dielectric surface is exposed to the electrolyte of interest, electrolyte/oxide

* Corresponding author. Tel.: +52-222-2663100; fax: +52-222-2470517.
*E-mail address*: jmolina@inaoep.mx

1876-6196 
doi:10.1016/j.proche.2012.10.136

interface potentials are able to modulate the transistor's conduction channel and therefore, its drain current and/or threshold voltage, being these parameters dependent on the pH of the solution.

The ISFET structure is obtained by using commercially available sub-micron Complementary Metal-Oxide-Semiconductor (CMOS) fabrication technology so that development of integrated ISFET sensors along with integrated pseudo-reference electrodes using standard and fully-compatible microelectronic processing/materials is possible. At the heart of this sensor, lies the final passivation surface material which is deposited atop one of the MIM structures (which in turn is connected in series to the gate of the MOSFET device) via the last metallization layer. By modifying the density of reactive sites present at the surface of this passivation layer, the effective chemisorption of the ions being detected at this surface is translated into a modulation of the inversion charge density at the silicon channel of the MOSFET device. By using these devices to measure the pH of buffer solutions, we notice a corresponding relationship between the pH of the solutions and the current-voltage (I-V) characteristics of the MOSFET devices, obtaining larger sensitivities to pH when they are operated close to sub-threshold conduction instead of strong-inversion regime. Finally, fabrication of these sensors by using a Low-Voltage Low-Power (LVLP) CMOS-based technology paves the way to integrate additional electronics within the same chip so that more intelligent functions (data acquisition and processing, memory, etc.) for these devices could be developed in order to produce low-cost, dispensable and portable sensors for specific biomedical applications.

## 2. Experimental

A Low-Voltage Low-Power (LVLP) 0.25µm CMOS-based technology was used for fabrication of ISFET sensors on silicon. For this work, we used the so-called M22W technology, which is proprietary of *Freescale Semiconductor*. A schematic of the MOSFET/MIM structure is shown in figure 1(a), where the area encircled by a dashed line encloses the sensing plate (SP) and the reference electrode plate (RE).

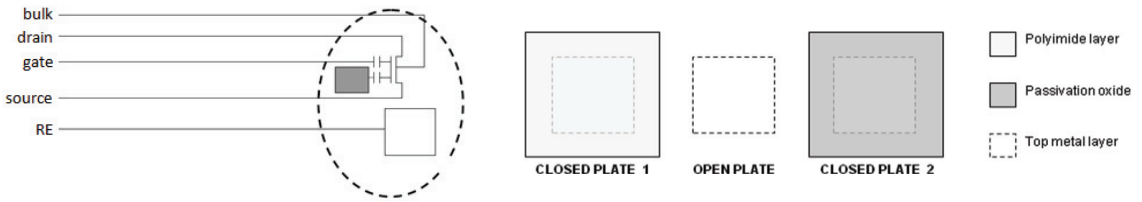


Fig. 1. (a) Physical distribution of the MOSFET electrical contacts and its sensitive plates (SP/RE plates) within the chip area; (b) Top-view of the available SP/RE configurations.

Those surface areas (from both SP/RE plates) will be directly exposed to the chemical solutions to be measured. Additionally , in order to ensure adequate aluminum wiring from chip to printed circuit board (PCB), all the wiring was manually encapsulated by casting and curing epoxy-resin so that safe pH electrochemical testing could be realized (thus avoiding short-circuits when measuring highly ionic solutions). Electrical I-V and electro-chemical I-V-pH measurements were done with an HP 4156B Semiconductor Parameter Analyzer and buffer solutions with pH= 4, 7 and 10, so that a broad range of ionic activity for the hydrogen species could be measured with these sensors. Some chips were subjected to a hot-plate (HP)-based baking at 100-200°C in air in order to restore the original I-V characteristic for some of the devices under test. Figure 1(b) is a schematic of the different configurations used for both the SP/RE plates. A closed plate being the last metal layer completely covered by a) thick polyimide or b)

only the passivation oxides, while the open plate is the metal being completely exposed to the environment. In this work, only the CLOSED PLATE 1 (CP1) and OPEN PLATE (OPEN) configurations for the SP/RE plates were tested. Since the open plate exposes the top metal layer (AlSi-2% alloy) to oxygen present in the atmosphere, uncontrolled oxidation of this metal is expected so that a thin layer of alumina ($Al_2O_3$) based oxide could be present at its surface. This is important since $Al_2O_3$-based ISFETs shows almost ideal Nernstian response of ~60mV/pH [1]. However, even with a high-sensitive surface, its oxidation mechanism is non-linear thus preventing reproducible pH electrochemical measurements.

## 3. Results and discussion

### *3.1. pH Sensitivity of a Sensing Plate having a CP1 configuration*

For a SP having a CP1 surface, the thick (~9µm) polyimide/oxide passivation layers prevents the hydrogen ions to interact with a supposedly thin layer of $Al_2O_3$ formed at the top metal surface. Nevertheless, a weak interaction of the pH buffer solutions with the electrical Id-Vg characteristic of this device can be seen. Electro-chemical I-V-pH measurement results are shown in semi-log and log-log formats in figure 2(a-b). Even though figure 2(a) shows some Id response to pH, the change in Id is quite small considering the 6 decades of pH being tested. For Vg=0.6V, Id changes slightly around 1e-5A/um. In order to better grasp the MOSFET Id sensitivity to pH, a log-log plot is better suited so that wider Id windows can be observed for the same Vg applied, see figure 2(b). There, it is clearly seen that the MOSFET Id sensitivity to pH can be enhanced by operating the device well below sub-threshold region, where Id could change within an order of magnitude. On the other hand, the saturation region shows almost no change in Id to pH buffer solution. By taking Id lectures at a fixed gate voltage (Vg=0.6V) it is possible to summarize the sensitivity of this sensor when different $V_{REF}$ biasing conditions are applied.

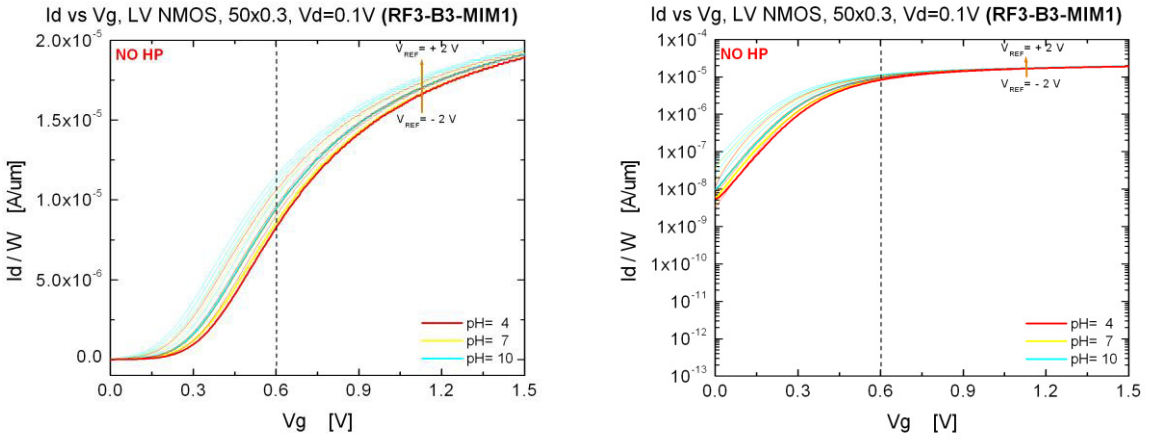


Fig. 2. (a) I-V-pH curves plotted in semi-log format showing a weak Id response to pH=4, 7, 10. (b) Same I-V-pH curves plotted in log-log format. At below/above Vg=0.6V, two different sensitivity spectrums are clearly seen for this later plot. For each pH measured, $V_{REF}$ was also changed from -2V to +2V in order to obtain some dependence of the sensor response to this voltage.

Figure 3(a) shows that even for different $V_{REF}$ applied (voltage applied to RE), Id shows no response to pH. Even though the sensitivity of Id to pH is shown for the Vg=0.6V condition only, it is clearly seen that Id readings before any pH measurement (NO BUFFER) will practically produce the same behavior

compared to actual pH-measurement readings. This particular sensor was obtained from a particular wafer batch (RF3). A second batch (RF4, having a different layout and thus, processing) contains the same CP1 configuration for the SP structures as well, so that by applying the same biasing and measuring conditions for all CP1 devices found in both chips, we can obtain the data shown in figure 3(b). There, we summarize the Id sensitivity to pH for different devices having the same CP1 structure.

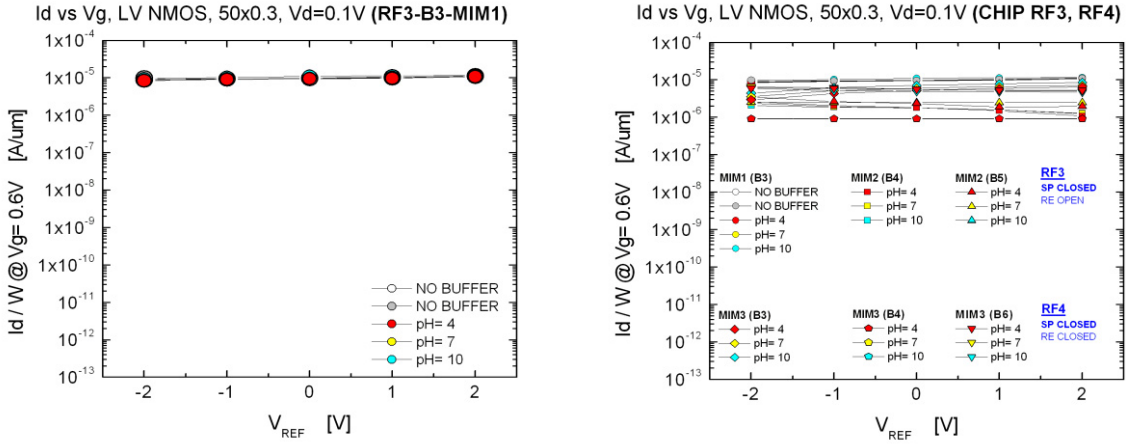


Fig. 3. (a) Id/W readings (normalized to the W of the transistor) taken at Vg=0.6V for measurements out and within pH buffer solutions and for different $V_{REF}$ biasing conditions. (b) Summary of some Id/W readings taken at Vg=0.6V for all tested MOSFET/MIM structures having sensing plates with the CP1 configuration and for different $V_{REF}$ biasing conditions.

In fig. 3(b), and in spite of the Id distribution between 1-10μA/μm for all different measured devices, the bottom line is that a poor sensitivity response to pH will be obtained for SP having CP1 structures. In order to overcome this lack of sensitivity, one can operate this sensor at well below sub-threshold biasing conditions or we can use a different configuration for the SP, in this case, an open configuration, OPEN.

### *3.2. pH Sensitivity of a Sensing Plate having an OPEN configuration*

This device has a configuration where the surface of the SP's top metal is directly exposed to the atmosphere and thus, quite prone to oxidation such that a thin $Al_2O_3$ film will develop at its surface. Since we do not have direct electrical access to any SP, and because a surface oxidation process is difficult to measure/control, any possible sensitivity to pH for this device will be extremely difficult to reproduce/ control (worst case would be having a variable sensitivity characteristic for repetitive measurements within the same pH buffer levels) and even this parameter will change by chemical surface modification processes [3]. Nevertheless, and compared to the former SP-CP1 configuration, a SP-OPEN device shows much better response to pH solutions. Before that, we want to notice that the SP-OPEN structure is quite prone to processes similar to irregular charging/discharging of a MIM capacitor, with the final effect being shifting the threshold voltage Vth and other MOSFET parameters as well. Figure 4(a) shows three different measurement results: the black line is the initial I-V data for that particular device, which, after being wired-to-PCB, encapsulated with epoxy-resin and stored for some weeks within a Petri-dish, a new measurement showed a huge positive shift in Vth (light-gray lines); a third data set (green lines) is another measurement for the same device after being thermally-annealed atop a hot-plate (HP) in air at 200°C. Good Vth recovery is clearly seen after heating when compared to the initial I-V characteristics.

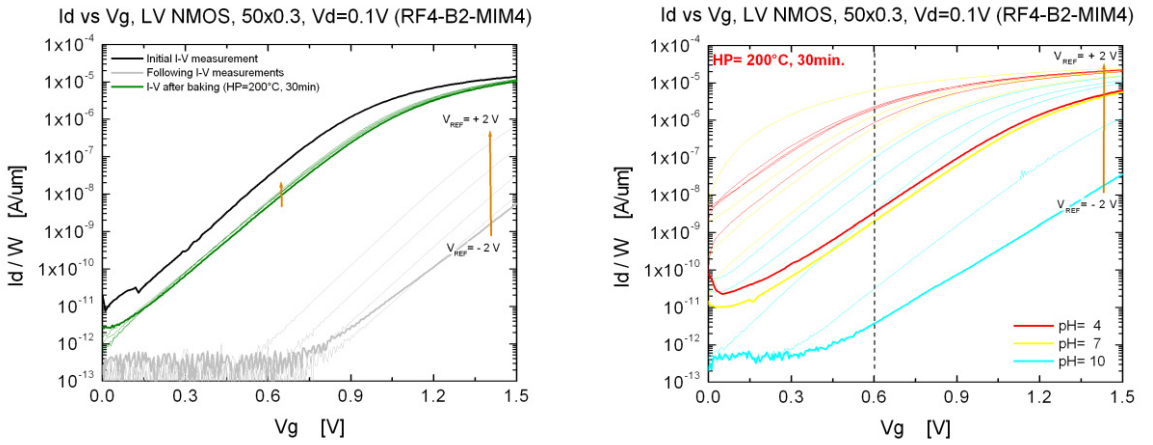


Fig. 4. (a) I-V experimental data for an SP-OPEN device measured after 3 different conditions: initial (black line), charged (gray lines) and recovered (green lines). A short HP-baking (200°C, 30min) is applied in order to recover the I-V characteristics. (b) I-V-pH curves plotted in semi-log format showing a large Id response to pH=4, 7, 10 and for different $V_{REF}$ biasing conditions. At below/above Vg=0.6V, almost the same wide sensitivity spectrums of Id(pH) are seen.

Once the ΔVth problem has been temporarily solved, we immediately measure pH buffer solutions with the recovered device so that proper readings can be obtained and analyzed. Electro-chemical I-V-pH measurement results are shown in semi-log format in fig. 4(b). Compared to the SP-CP1 configuration, a SP-OPEN sensor shows wider changes in Id for the whole range of pH measured (Id changes by about 3-4 orders of magnitude for the whole pH range being tested). In this figure, the largest changes in Id for different pH buffer solutions as well as for different $V_{REF}$ biasing conditions are simultaneously obtained. For all curves in fig. 4(b), biasing the $V_{REF}$ terminal from -2V to +2V while measuring the sensor's I-V characteristics within a pH buffer solution, will exert a huge influence on the final transistor's Id levels. This is similar to a body or substrate bias effect on the MOSFET's Vth. The difference being that for negative/positive $V_{REF}$ biasing, there will be positive/negative shifts in Vth respectively, which is opposed to the negative/positive shifts in Vth expected for a substrate bias condition. This is expected to some extent since $V_{REF}$ is applied to a RE metal plate, which is the top metal of the device, instead of being directly applied to the substrate. Therefore, the $V_{REF}$ bias can be thought as an electric field originated above the inversion channel (instead below this channel when $V_{BULK}$ is normally used to shift Vth) and whose field lines still influence the channel formation. On the other hand, we notice that the greater sensitivity lies in solutions within a pH=10 to 7 (alkaline solutions). This is advantageous since we want to use these devices for medical applications where important human fluids like blood, normally have pH levels slightly alkaline pH= 7.35-7.45 [3]. Other fluids like saliva and urine have pH levels lying between 7.4-6.0 and 6.0 respectively, so that full sub-threshold region operation could be better suited. Also, the initially high sensitivity found in sub-threshold region is reduced in saturation. This effect is clearly seen at Vg≥1.0V, where Id(pH) is limited with increasing Vg. From fig. 4(b), the sensitivity has been extracted at Id=1nA/um and by taking into account the pH range of interest as well. We notice a sensitivity S= 205, 218 and 143 mV/pH (for pH between 7 and 10 only) when $V_{REF}$ is biased with -2, -1 and 0V respectively. Normally, the expected S for an ISFET device is at most, ~60mV/pH [1]. In our case, the combined effect of having a SP-OPEN configuration (therefore producing a surface which is continuously modified in the chemical sense) and the sensitivity extraction mostly within the sub-threshold region will produce these

large values for S. Figures 5(a-b) below, summarize the Id response to pH for two specific operating regions of the ISFET: sub-threshold and saturation, Id is taken at Vg= 0.6 and 1.2 V respectively.

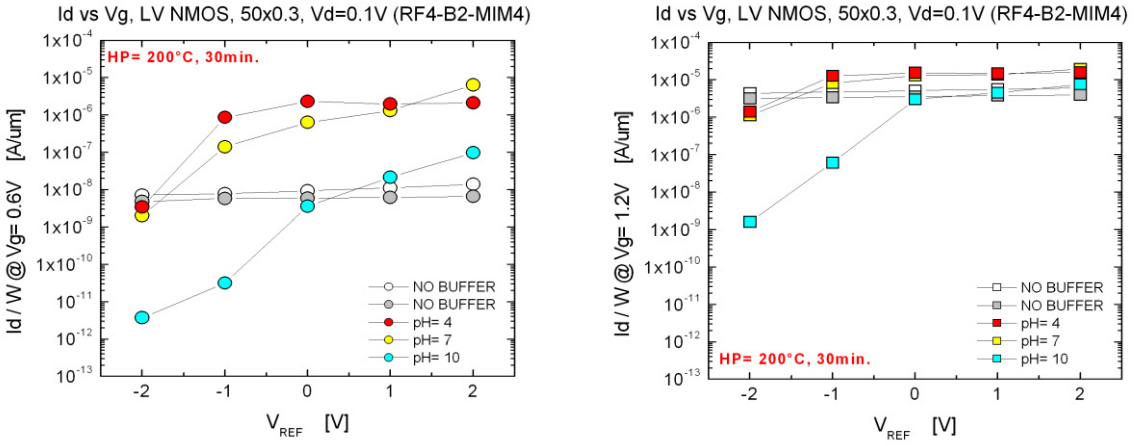


Fig. 4. (a) I-V experimental data for an SP-OPEN device measured after 3 different conditions: initial (black line), charged (gray lines) and recovered (green lines). A short HP-baking (200°C, 30min) is applied in order to recover the I-V characteristics. (b) I-V-pH curves plotted in semi-log format showing a large Id response to pH=4, 7, 10 and for different $V_{REF}$ biasing conditions. At below/above Vg=0.6V, almost the same wide sensitivity spectrums of Id(pH) are seen.

For both figures, it is clear that $V_{REF}$ is able to modulate the Id response to pH of the device. Using $V_{REF}$= -2V to 0V, we find the largest change in Id taken at those Vg readings. For the near sub-threshold condition (Vg=0.6V), the change in Id with pH is almost constant for all $V_{REF}$ applied, producing at maximum, a change in Id of five orders of magnitude for all six decades of pH being tested. On the other hand, the saturation or strong inversion condition (Vg=1.2V) produce at maximum, a change in Id of three orders of magnitude for the whole range of pH when $V_{REF}$=-2V only. If $V_{REF}\geq$0V, this response suddenly drops to almost no sensitivity whatsoever. The largest Id response to pH is then found when the device is operated at sub-threshold. This is important since the highest sensitivity along with the lowest power consumption can be obtained simultaneously. For large-channel MOSFET devices, the quadratic dependence of Id versus Vg ($Id\alpha Vg^2$) no longer holds for submicron MOSFET devices where Id versus Vg now produces a linear dependence in saturation region [4]. For both long-channel and submicron MOSFET devices however, the sub-threshold region provides an exponential dependence of Id versus Vg ($Id\alpha e^{Vg}$) so that using this region for increasing the sensitivity of these kind of sensors is important in view of the many benefits it provides. For this region, the only precaution is the proper biasing of Vds in order to avoid the already known short-channel effects on sub-threshold swing which produce different slopes for this important parameter (i.e., *punchthrough*).

## 4. Conclusions

Integration of MOSFET/MIM devices along with SP/RE structures for pH chemical detection was demonstrated using a 0.25µm CMOS-based process. A SP-CP1 based sensor presents poor sensitivity to pH independently of the $V_{REF}$ applied whereas a SP-OPEN based sensor presented the highest Id response to pH and this high sensitivity could be modulated by biasing $V_{REF}$. For both SP structures it is clearly demonstrated that sub-threshold conduction regime provide greater sensitivities (compared to saturation

regime) along with the lowest power consumption. Finally, fabrication of these sensors by using a LVLP CMOS-based technology paves the way to integrate additional electronics within the same chip so that much more intelligent stages (data acquisition and processing, conditioning, calibration, memory, etc.) for these devices could be developed in order to produce low-cost, dispensable and portable sensors for specific *on-site* medical applications.

## Acknowledgements

This work was fully supported by the Mexican Council of Science and Technology (CONACYT-Mexico) and *Freescale Semiconductor Corporation,* Mexico-USA.

## References

1. P. Bergveld, Development of an ion-sensitive solid state device for neurophysiological measurements. *IEEE Transactions on Biomedical Engineering*, BME-17 (1970), pp. 70-71.
2. A. Van Den Berg, P. Bergveld, D.N. Reinhoudt and E.J. Sudhölter, Sensitivity control of ISFETs by chemical surface modification. *Sensors and Actuators*. **8** (1985), pp. 129-148.
3. *Merck Manual of Diagnosis and Therapy*. Avail., Online at http://www.merckmanuals.com/professional/index.html
4. S. Wolf, *The Submicron MOSFET*, Lattice Press (1996).